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Published in:
Salt Weathering on buildings and Stone Sculptures

Publication date:
2011

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Paz-Garcia, J. M., Johannesson, B., Ottosen, L. M., Ribeiro, A. B., & Rodriguez-Maroto, J. M. (2011). Influence of the Chemical Interactions on the Removal Rate of Different Salts in Electrokinetic Desalination Processes. In *Salt Weathering on buildings and Stone Sculptures* (pp. 373-380). University of Cyprus.

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Influence of the Chemical Interactions on the Removal Rate of Different Salts in Electrokinetic Desalination Processes

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ABSTRACT

Electrokinetic desalination techniques have been successfully applied for the prevention of salt-induced deterioration problems of masonry and other construction materials. A mathematical model for electrochemical desalination treatments is described, based on the Poisson-Nernst-Planck system of equations and accounting for the chemical interactions between the species in the pore solution and the solid matrix. Due to their high abundance in the natural environment, chlorides, nitrates and sulfates are considered the main ions responsible to the salt decay processes in buildings materials and sculptures. Simulations of the desalination treatment of brick samples contaminated with these target contaminants are shown. The influence of the chemical interactions on the efficiency is highlighted in the results.

Keywords: Electrokinetic desalination, chemical equilibrium, extent of the reaction, reactive transport, Poisson-Nernst-Planck system

1 INTRODUCTION

Due to their abundance in the natural environment, chlorides, nitrates and sulfates are considered the main responsible for salt-decay weathering processes in buildings materials and sculptures (Ottosen et al. 2008a, Goudie & Viles 1997). Electrokinetic desalination techniques have been successfully applied for the prevention of salt-induced deterioration processes in masonry and other construction materials. The technique consists of the transport of the damaging salts out of the porous material in an externally applied electric DC field. Experimentally, the enhancement of the technique using a buffer substance at the electrode compartments has been shown to raise the effectiveness, in terms of increasing the removal rate and reducing the energy consumption. Furthermore, the buffer substance enhancement avoids undesirable side effects on the material being desalinated, such as the dissolution of the solid matrix due to the sharp pH changes produced at the electrodes (Ottosen & Rodig-Dalgaard 2009).

Despite the fact that the ionic mobility coefficients of chlorides, nitrates and sulfates ions are very similar, experimental results for electrokinetic desalination treatments have shown different removal efficiency for each species (Ottosen et al. 2008b). These differences can be

explained by the chemical interactions taking place between the species in the pore solution and the solid matrix. Therefore, the specific chemical reactions that can take place during the process must be taken into account when optimizing or modeling electrokinetic desalination treatments (Ottosen et al. 2008a; Ribeiro & Rodriguez-Maroto 2005). Some aspects affecting related to the chemical reactivity of the system during the electrokinetic treatment are:

- Species in the system migrate with different transport rates. As consequence, a displacement in the chemical equilibrium is produced. For instance, protons move faster than hydroxide ions, and the water auto-ionization reaction will proceed to keep the equilibrium. This feature has to be taken into account even in free diffusion models.
- The electrical current is transformed into an ionic current by means of the electrochemical reactions taking place at the electrodes. Due to water electrolysis reactions, in non-amended treatments severe pH changes are expected with serious implications on the chemical speciation in both the pore solution and the solid matrix.
- Ions migrate towards the electrode with opposite charge producing fronts with sharp gradient of concentration. When fronts collide, located precipitation may occur.

In this work, a model for the reactive transport in electrokinetic processes is described. Numerical simulations of the electrokinetic desalination of a brick sample contaminated with salts containing those target ions are shown. In the modeled system, the electrode compartments are considered filled with clay rich in pure calcite. The model includes the competition of different electrochemical reactions at the electrodes, as well as a feasible set of chemical equilibrium reactions describing the chemical reactivity.

Results from simulations demonstrate the influence of the chemical interactions affecting the target ions on the removal rate of those common salts. It can, therefore, be useful when designing full-scale desalination treatments.

2 MATERIALS AND METHODS

The model for the reactive transport in electrokinetic processes presented here has been designed as the combination of two strongly coupled modules: One for the transport process and another one for chemical equilibrium calculations. Both modules are described separately.

2.1 *The transport process*

In electrokinetic processes, ionic and non-ionic species migrate through the porous structure by a combination of different transport contributors (Ribeiro & Rodriguez-Maroto 2005). The transport process is modeled based on the Nernst-Planck-Poisson (NPP) system of equations (Pamukcu 2009, Johannesson & Ottosen 2008). A detailed description of the finite element integration of the NPP system of equations can be found in (Paz-Garcia et al. 2011a). The system presented here has been extended in order to include the transport of water due to electroosmotic and capillary suction forces and the corresponding advective flow of the species in the pore solution. In addition to this, the system has been coupled with a chemical equilibrium module, in order to take into account the chemical reactions during the transport process. Porosity changes due to the precipitation and dissolution reactions during the process

are monitored, and the effective transport coefficients are calculated taking into account the variation of the porosity along the material.

The transport of mass along the porous media is described by means of the corresponding mass continuity equation of each chemical species involved in the system:

$$\frac{\partial n_i}{\partial t} = -\nabla \mathbf{J}_i + G_i \quad (1)$$

where the $n_i \equiv [\text{mol} \cdot \text{kg}_w^{-1}]$ is the molal concentration of each chemical species i , G_i is the generation term and \mathbf{J}_i is the flux term, described as:

$$\mathbf{J}_i = - \left(\underbrace{n_i w^{-1} D_w \nabla w}_{\text{total moisture transport}} + \underbrace{k_e n_i \nabla \phi}_{\text{electroosmosis}} + \underbrace{D_i^{\text{eff}} \nabla n_i}_{\text{diffusion}} + \underbrace{U_i^{\text{eff}} n_i \nabla \phi}_{\text{electromigration}} \right) \quad (2)$$

where D_i^{eff} is the effective diffusion coefficient, ϕ is the electrical potential, U_i^{eff} , is the effective ionic mobility coefficient, $w \equiv [\text{kg}_w \cdot \text{m}_{\text{pore}}^{-3}]$ is the porous moisture content i.e. the amount of water filling the pore structure and k_e is the electroosmotic permeability coefficient. D_w is the moisture diffusivity coefficient in the solid matrix under consideration and it represents the transport of water due to the gradient of moisture content. This term describes the total moisture transport in both vapor and liquid phases, as a combination of diffusion, viscous saturated flow and capillary transport, assuming isothermal conditions (Johannesson & Janz 2009)

Effective diffusion coefficients are calculated from the corresponding diffusivity at infinite solution and the porosity, p , and tortuosity, τ , of the porous media and the Nernst-Townsend-Einstein relation relates the ionic mobility coefficient to the diffusivity (Paz-Garcia et al. 2011a). The Poisson's equation in electrostatics is used to complete the strongly coupled NPP system of equations.

$$\varepsilon \frac{\partial^2 \phi}{\partial x^2} = F \sum_{i=1}^M n_i z_i \quad (3)$$

where $\varepsilon = \varepsilon_r \varepsilon_o$ is the water permittivity, ε_o is the vacuum permittivity and ε_r is the water relative permittivity, F the Faraday constant and z_i is the ionic charge. The Poisson's equation acts as a charge balance, used to calculate the electrical potential from the charge density in each point of the solution. The strongly coupled character of the system assures the electroneutrality condition in the global system.

2.2 Chemical equilibrium

During the transport process, chemical species may react with other species in the solution and with the solid matrix. Modeling of this reactive transport accounting for chemical reaction has severe numerical difficulties, mainly due to the huge difference of orders of magnitude of reactions and transport rates. In general, it can be assumed that most of the reversible chemical reactions taking place in the process are fast enough to reach the equilibrium. According to this, for a selected set of reversible chemical reactions, the reactive transport can be modeled under

the assumption of instantaneous chemical equilibrium. Only irreversible, slow reversible reactions and the electrochemical reactions at the electrodes are considered time dependent.

In the present work, the Newton-Raphson method for re-establishing the chemical equilibrium condition described in (Paz-Garcia et al. 2011b) has been coupled with the transport module. The model deals simultaneously with aqueous and precipitation/dissolution reactions, accounting for the saturation index of the solids in each iteration and each point. In addition to this, the difference between the rate of precipitation/dissolution reactions and those involving only aqueous species has been taken into account. A line search approach is used in the Newton Raphson method to assure the convergence and, the same time, deal with the non-negative concentration constraints of all the chemical species.

2.3 The modeled system

The desalination of a single brick contaminated with a combination of KCl, KNO₃ and K₂SO₄ is studied. Figure 1 shows a schematic representation of the experimental setup, based on the cases studied in Ottosen & Rodig-Dalgaard 2009 and Ottosen et al. 2008b. A brick piece of 10 cm length and 125 cm² cross sectional area is suggested to a constant current of 10 mA during 7 days. A buffer substance enhanced electrokinetic treatment is assumed, based on the buffer capacity of CaCO₃. Cylindrical electrode compartments filled with clay poultice rich in CaCO₃ are placed at each end of the brick sample. The cylinders are 5 cm length and 8 cm of internal diameter. The distance between the electrodes and the brick surface is 4 cm.

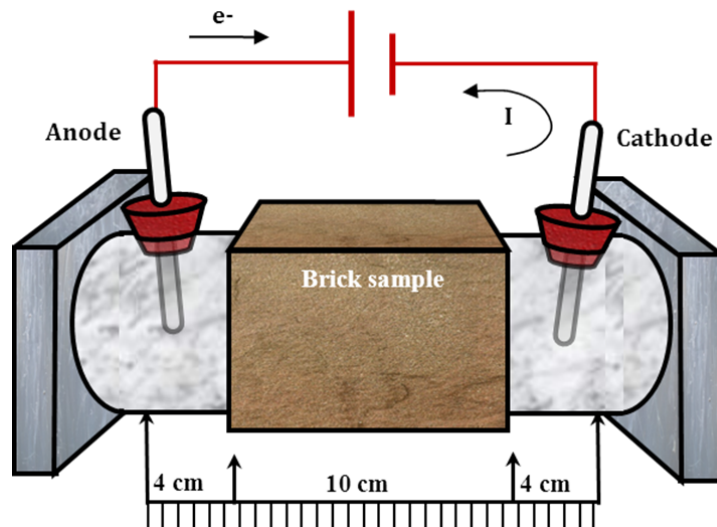


Figure 1: Schematic representation of the experimental setup for the electrodesalination of a brick.

The brick is considered as a porous inert matrix with a certain amount of CaCO₃ per unit volume (yellow brick). The carbonated clay in the electrode compartments initially has 1 mol/m³ of each salt, which gives the pore solution sufficient conductivity in order to develop the necessary ionic current in the electrokinetic process. Table 1 collects the initial solid composition of the brick and the clay in the simulations. The units are referred to the considered constant volume of the heterogeneous matrix, i.e. volume of solid plus pore.

Table 1. Characteristics of the solid matrices

Property	Brick	Clay
Inert solids	17500 mol/m ³	5000 mol/m ³
CaCO ₃ (s)	100 mol/m ³	10000 mol/m ³
KCl (s)	50 mol/m ³	1 mol/m ³
KNO ₃ (s)	50 mol/m ³	1 mol/m ³
K ₂ SO ₄ (s)	50 mol/m ³	1 mol/m ³
Initial porosity	0.2963	0.4307
Cross sectional area	125 cm ²	50 cm ²
Length	10 cm	2 × 4 cm

Table 2 shows the set of reversible chemical reactions selected for the simulation and Table 3 shows the set of dissolution/precipitation reactions that completes the system. The equilibrium constants or solubility products, obtained from (Parkhurst & Appelo, 1999), were adapted in order to be consistent with the given stoichiometric. For the sake of simplicity, only potassium is considered as a common counterion for the target contaminants. Nevertheless, the use of the CaCO₃ forces to consider calcium as a secondary counterion.

Table 2. Set of aqueous chemical reactions

	log ₁₀ (K _{eq})		log ₁₀ (K _{eq})
OH ⁻ ⇌ H ₂ O – H ⁺	14.00	CaCl ⁺ ⇌ Ca ⁺² + Cl ⁻	0.29
CaCO ₃ ⇌ Ca ⁺² + CO ₃ ⁻²	-3.22	CaSO ₄ ⇌ Ca ⁺² + SO ₄ ⁻²	-2.31
HCO ₃ ⁻ ⇌ H ⁺ + CO ₃ ⁻²	-10.33	KCl ⇌ K ⁺ + Cl ⁻	0.50
CO ₂ + H ₂ O ⇌ H ⁺ + HCO ₃ ⁻	-16.68	KNO ₃ ⇌ K ⁺ + NO ₃ ⁻	0.15
CaHCO ₃ ⁺ ⇌ Ca ⁺² + H ⁺ + CO ₃ ⁻²	-11.43	KSO ₄ ⁻ ⇌ K ⁺ + SO ₄ ⁻²	-0.88
CaOH ⁺ ⇌ Ca ⁺² + H ₂ O – H ⁺	12.78	KOH ⇌ K ⁺ + H ₂ O – H ⁺	14.46
CaNO ₃ ⁺ ⇌ Ca ⁺² + NO ₃ ⁻	-0.60	HSO ₄ ⁻ ⇌ H ⁺ + SO ₄ ⁻²	-1.98
Ca(NO ₃) ₂ ⇌ Ca ⁺² + 2NO ₃ ⁻	-0.50		

Table 3. Set of precipitation/dissolution chemical reactions

Solid reactions	log ₁₀ (K _{sp})
CaCO ₃ (s) ⇌ Ca ⁺² + CO ₃ ⁻²	-8.48
KCl (s) ⇌ K ⁺ + Cl ⁻	0.87
CaCl ₂ · 6H ₂ O (s) ⇌ Ca ⁺² + 2Cl ⁻ + 6H ₂ O	3.94
KNO ₃ (s) ⇌ K ⁺ + NO ₃ ⁻	-0.10
Ca(NO ₃) ₂ (s) ⇌ Ca ⁺² + 2NO ₃ ⁻	5.98
K ₂ SO ₄ (s) ⇌ 2K ⁺ + SO ₄ ⁻²	-1.85
CaSO ₄ · 2H ₂ O (s) ⇌ Ca ⁺² + SO ₄ ⁻² + 2H ₂ O	-4.61
KOH (s) ⇌ K ⁺ + H ₂ O – H ⁺	24.6
Ca(OH) ₂ (s) ⇌ Ca ⁺² + 2H ₂ O – 2H ⁺	22.81

3 RESULTS AND DISCUSSION

Figure 2 shows the concentration profile of the target contaminants (Cl^- , NO_3^- and SO_4^{2-}) in the desalination treatment. As expected from the experimental results (Ottosen et al. 2008b) the transport of the target anions towards the anode differs. The concentration of SO_4^{2-} in the brick seems to decrease faster than the other ions. Nevertheless, the accumulation of SO_4^{2-} in the anode compartment is significantly lower than the other two anions.

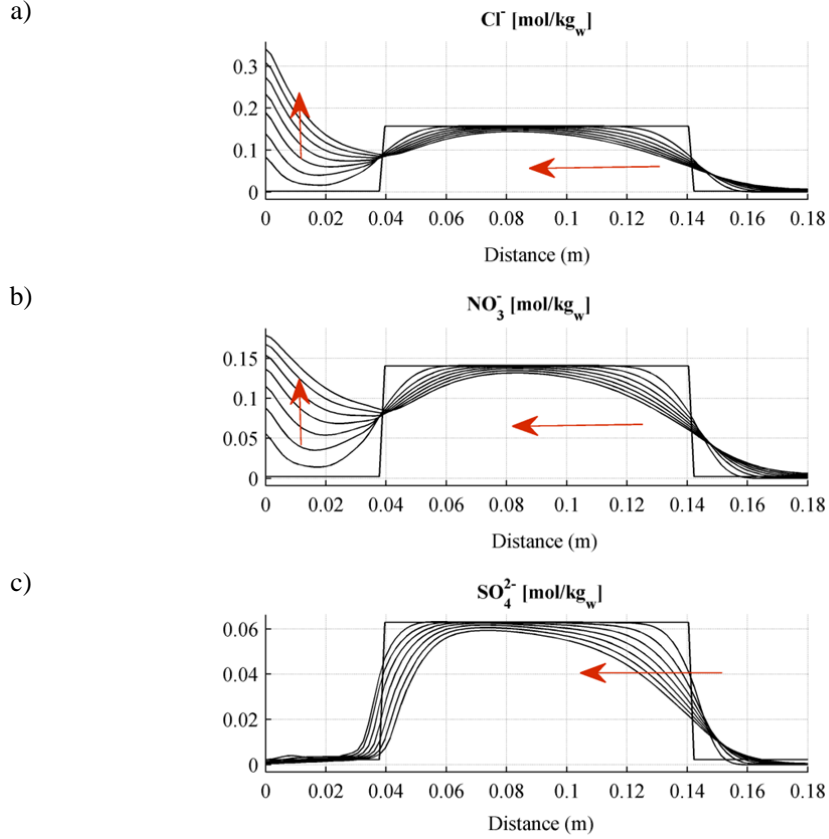


Figure 2. Concentration profile of the target ions along the sample. One profile every 24 h.

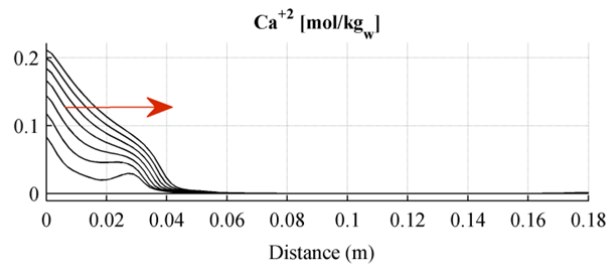


Figure 3. Calcium front developed in the cathode compartment. One profile every 24 h.

Figure 3 shows the calcium front developed at the anode compartment as result of the calcite dissolution in the buffering process. As a cation, calcium migrates towards the cathode going through the brick. Calcium may react with the different species in the system during its migration.

Table 2 and Table 3 collect a number of chemical reactions involving calcium and the target ions. Depending on the saturation index, some precipitates can be formed, being gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) the more insoluble in the set of reactions defined. Figure 4 shows the final distribution of solids, in volume fraction units; being the porosity the difference the rest of the volume not occupied by the solids. It can be seen that the electrolysis reaction at the anode produces a strong dissolution of the calcite at the electrode compartment, which matches with the calcium front shown in figure 3. The simulation does not predict the precipitation of calcium hydroxide in the cathode compartment. Furthermore, a significant precipitation of gypsum is observed in the region near nearby the anode compartment and the brick interface, where the calcium front and the sulfate front collide.

According to the results from the simulation presented here, the chemical interaction of calcium with respect the target anions can be assumed the main responsible of the differences between the removal rate of SO_4^{2-} compared to Cl^- and NO_3^- .

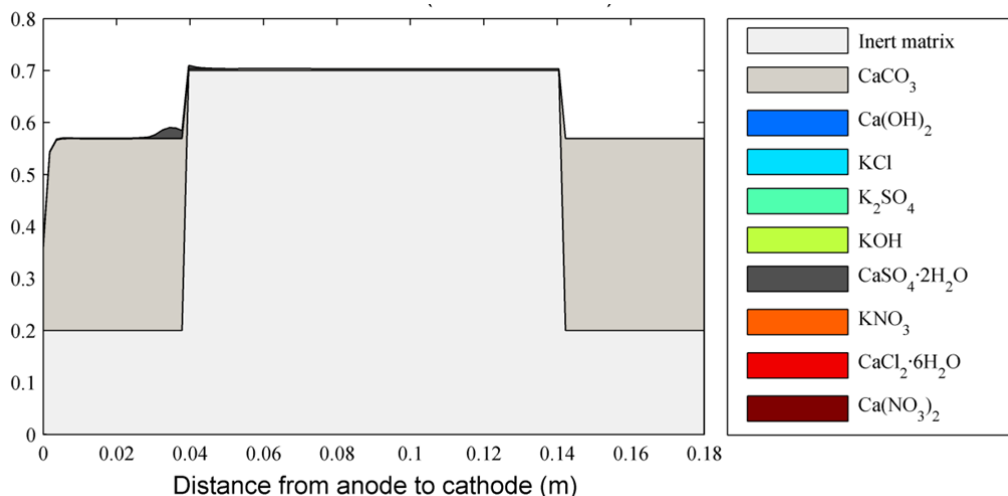


Figure 4. Distribution of solids (volume fraction) after 7 days of treatment.

4 CONCLUSIONS

A model for the reactive transport in electrokinetic desalination treatments has been described. Results from simulations show that the efficiency of the electrokinetic desalination treatments is different for each target ions, Cl^- , NO_3^- and SO_4^{2-} , using K^+ as counterion. Chloride is the fastest anion to be removed, whereas the sulfate is significantly slower. These differences are explained by the specific chemical reactivity of the ions.

In the case of the electrodesalination treatment modeled here, the enhancement by using calcium carbonate as buffer substance in the electrode compartments is considered. As result, the acid

front developed in the anode compartment is to some extent replaced by a calcium front that may proceed towards the cathode by electromigration. The reactivity of calcium with the target anions is consistent with the results obtained in the simulations. Calcium forms insoluble salts with sulfates that can limit the removal process, but also be hazardous for the material if a sharp precipitation is produced in the section where the calcium front matches the sulfates inside the sample, that could add to the salt decay of the material itself. Thus, this point is investigated experimentally at present.

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